CHAPTER – IV

DISCUSSION

CONTENTS

4.1 EFFECT OF pH

The effect of pH on photocatalytic degradation of dyes has been studied. The observations are reported in Tables 3.2, 3.7, 3.12, 3.17, 3.22 and 3.27. The optimum value of pH was observed as 7.0, 9.5, 8.5, 8.5, 7.5 and 8.0 for Azure A, Evans blue, Rose Bengal, Methylene blue, Rhodamine B and Alizarin red-S, respectively.

It has been observed that the rate of photocatalytic degradation of the dyes (Azure A, Evans blue, Rose Bengal, Methylene blue, Rhodamine B and Alizarin red-S) increases as pH was increased. On further increasing the pH above a particular value, rate of the reaction was decreased. This may be explained by increase in attraction between cationic dye molecules (Azure A, Methylene blue and Rhodamine B) and hydroxyl ions as pH was increased, and accordingly, the rate of photocatalytic degradation of the dye increases. Above an optimum pH, a decrease in the rate of photocatalytic degradation of the dye was observed, which may be due to the fact that cationic form of dye molecules is converted in its neutral form, which faces almost no attraction towards the negatively charged semiconductor surface. Hence, the rate was retarded. But in case of anionic dyes (Rose Bengal, Evans blue and Alizarin red-S) the dyes will start facing a force of repulsion between anionic dyes and negatively charged surface of the graphitic carbon nitride. As a result, the rate of degradation decreased.

4.2 EFFECT OF DYE CONCENTRATION

The effect of concentration on their photocatalytic degradation has been studied. The observation are reported in Tables 3.3, 3.8, 3.13, 3.18, 3.23 and 3.28. The optimum value of dye concentration was observed as 1.00×10^{-4}, 1.00×10^{-4}, 0.8×10^{-4}, 1.5×10^{-4} ,0.8×10^{-3} and 3.2×10^{-3} M for Azure A, Evans blue, Rose Bengal, Methylene blue, Rhodamine B and Alizarin red-S, respectively.

The rate of photocatalytic degradation of dye was found to increase on increasing the concentration of dye. It may be due to fact that as the dye concentration was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate of degradation of the dye was observed. The rate of photocatalytic degradation was found to decrease with increase in the concentration of the dye further, which may be due to the fact that dye itself will start acting as a filter for

the incident radiations. It may not permit the desird light intensity to reach the surface of photocatalyst and hence, the rate of degradation was decreased.

4.3 EFFECT OF AMOUNT OF PHOTOCATALYST

The amount of photocatalyst also affects photocatalytic degradation of dye and therefore, its effect has been studied by varying the amounts of photocatalyst. The observations are reported in Tables 3.4, 3.9, 3.14, 3.19, 3.24 and 3.29. The optimum value of amount of photocatalyst was found as 0.08, 0.10, 0.08, 0.16, 0.12 and 0.12 g for Azure A, Evans blue, Rose Bengal, Methylene blue, Rhodamine B and Alizarin red-S, respectively.

It was observed that the rate of reaction was increased with increase in amount of photocatalyst, graphitic carbon nitride. The rate of reaction shows a declining behaviour beyond a particular amount of photocatalyst. This may be due to fact that as the amount of photocatalyst was increased, its exposed surface area also increases resulting in enhanced rate of degradation. However, after a limiting value, any addition of photocatalyst will increase only thickness of its layer at bottom of the vessel and not the exposed surface area. In this case, multilayers are formed and as a result, the reaction rate decreases slightly, because multilayers permit the e^- h^+ recombination as particles of photocatalyst are in close contact. As a consequence, rate of degradation decreases.

4.4 EFFECT OF LIGHT INTENSITY

The light intensity affects photocatalytic degradation of dye and therefore. its effect has also been studied by variation of the intensity of light. The observations are reported in Tables 3.5, 3.10, 3.15, 3.20, 3.25, and 3.30. The optimum value of light intensity was observed as 70.0, 60.0, 70.0, 60.0, 60.0 and 70.0 m W cm^{-2} for Azure A, Evans blue, Rose Bengal, Methylene blue, Rhodamine B and Alizarin red-S, respectively.

It was observed that the rate of reaction was increased with increasing light intensity due to fact that the number of photons striking per unit area of the semiconductor per unit time also increases. However, at higher light intensities, some thermal side reaction may also start and hence, the rate of photocatalytic degradation was decreased on increasing the intensity of light further in some cases.

4.5 MECHANISM

The role of active oxidizing species was confirmed by using specific scavengers. It was observed that reaction rate was drastically reduced in presence of Isopropyl alcohol, which ascertained that hydroxyl radical played a major role in oxidative degradation of these dyes.

On the basis of these observation, a tentative mechanism for photocatalytic degradation of Azure A, Evans blue, Rose Bengal, Methylene blue, Rhodamine B and Alizarin red- S is proposed as-

$$^{1}Dye_0 \xrightarrow{h\nu} {}^{1}Dye_1 \quad ...(4.1)$$

$$^{1}Dye_1 \xrightarrow{ISC} {}^{3}Dye_1 \quad ...(4.2)$$

$$g\text{-}C_3N_4 \xrightarrow{h\nu} g\text{-}C_3N_4\,[h^+\,(VB) + e^-\,(CB)] \quad ...(4.3)$$

$$^{-}OH + g\text{-}C_3N_4\,(h^+) \longrightarrow {}^{\bullet}OH + g\text{-}C_3N_4 \quad ...(4.4)$$

$$^{\bullet}OH + {}^{3}Dye_1 \longrightarrow \text{Leuco Dye} \quad ...(4.5)$$

$$\text{Leuco Dye} \longrightarrow \text{Products} \quad ...(4.6)$$

The dye is excited to its first excited singlet state by absorbing a light of suitable wavelength. than, it is transferred to its triplet excited state by intersystem crossing (ISC). On the other hand the graphitic carbon nitride also absorbs light equivalent to its band gap.

As a consequence, an electron is excited from to its valence band to conduction band. The hole in the valence band of this photo catalyst abstracts and electron from hydroxyl ion by hole forming a hydroxyl radical.

This hydroxyl radical reacts with triplet state of dye to convert it to its leuco form, which is unstable. This leuco form is degraded to smaller fragments as products, which are almost harmless or less harmful such as Co_2, H_2O, inorganic ions, etc.

The order of rate of their photocatalytic degradation was found to be:

Azure A > Methylene blue > Evans blue > Rhodamine B > Alizarin red-S > Rose Bengal.

The use of a metal free semiconductor graphitic carbon nitride in the photocatalytic degradation of Azure A, Evans blue, Rose Bengal, Methylene blue, Rhodamine B and Alizarin red- S is welcome addition, as this process is ecofriendly in nature as it degrades organic pollutants into their less harmful or almost harmless counterparts such as CO_2, H_2O, and some inorganic ions, which can be easily removed by ion-exchange method. Time has come that such non-metallic photocatalyst may replace metal based photocatalyst in near future.

❐❐❐